Flow-Vacuum Pyrolysis of Polycyclic Compounds
25. Pyrolysis of 3-Benzylidene-Phtalide

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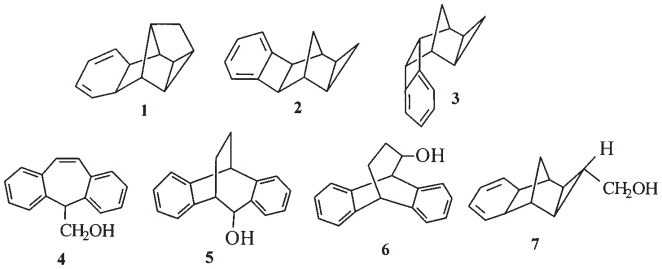
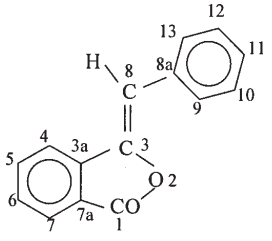
*Flow vacuum pyrolysis of 3-benzylidene-phtalide (**8**) at 1 Torr and between 300 - 950°C afforded as main reaction products: phenanthrene, anthracene, fluorenone and anthraquinone. A reaction mechanism including radicalic species is suggested in order to rationalize the formation of the reaction products.*

Keywords: flow-vacuum pyrolysis, benzylidenephtalide, radical reactions

In the previous papers of this series [1] we described the flow-vacuum pyrolysis of some benzo-annelated polycyclic hydrocarbons e.g. **1**[2], **2**[3], **3**[4] as well as of dibenzoannelated cyclic and polycyclic alcohols like **4**[5], **5**[6]**, 6**[7] and **7**[8]. In all cases we evidenced elimination reactions accompanied by rearrangement and aromatization processes.



In this paper we describe the results of flow-vacuum pyrolysis of the 3-benzylidene-phtalide (3-(phenylmethylene)-1(3H)-isobenzofuranone) (**8**)[9].



8

Experimental part

Melting points are uncorrected. The NMR spectra were registered on a Varian Gemini 300 apparatus at 300 MHz for ^{1}H and 75 MHz for ^{13}C, using TMS as internal standard. The IR spectra were registered on a Bruker Vertex 70 spectrophotometer.

Synthesis of 3-(phenylmethylene)-1(3H)-isobenzofuranone (3-benzylidene phtalide) (**8**)

The synthesis of compound **8** was performed according to [9] and the product analyzed by spectral methods:

IR spectrum (CCl_4, cm^{-1}): 685m; 760m; 868w; 911w; 967m; 1657w; 1765vi.

^{1}H-NMR spectrum ($CDCl_3$, δ ppm, J Hz): 6.28 (s, H^8); 7.12 (tt; 7.3; 1.3; 1H; H^{11}); 7.21 (t; 7.3; 2H; H^{10}; H^{12}); 7.37 (tt; 7.7; 1.0; H-6); 7.55 (td; 7.7; 1.0; 1H; H^5); 7.61 (dd; 7.7; 0.9; 2H; H^9; H^{13}); 7.63 (dd; 7.7; 2.7; 1H; H^4); 7.72 (dd; 6.8; 0.9; 1H; H^7).

^{13}C-NMR spectrum($CDCl_3$, δ ppm, J Hz): 166.95 (C^1); 144.41 (C$_q$); 140.43 (C$_q$); 134.61 (CH); 133.01 (C$_q$); 131.12 (C$_q$); 129.99 (CH); 128.88 (CH); 128.64 (CH); 128.33 (CH); 125.30 (CH); 123.07 (C$_q$); 119.94 (CH); 107.26 (CH).

Mass spectrum (m/z; relative abundance %): 50 (3); 89 (3); 164 (6);165 (8); 166 (5); 193 (7); 194 (8); 222 (100; B.P.; M); 223 (18; M+1); 224 (1; M+2).

Pyrolysis of 3-(phenylmethylene)-1(3H)-isobenzofuranone (3-benzylidene phtalide) (**8**)

The flow-vacuum pyrolysis of compound **8** was performed in a flow system using a previously described apparatus[5]. The pyrolysis quartz tube (40 cm length; 10 mm internal diameter) was filled with quartz chips of 3-5 mm on a 20 cm length; this zone was heated with a cylindrical electric oven. The temperature was continuously measured by a thermocouple and the pressure (~1 Torr) with a McLeod manometer. The compound sample (30 mg for analytical and 100 mg for preparative experiments) was sublimated under argon flow (4mL/min^{-1}) into the hot pyrolysis tube. The reaction products were accumulated as an oily liquid at the cooled end of the pyrolysis tube. The products were dissolved in CH_2Cl_2, the solvent was evaporated *in vaccum* and the residue (about 80- 85 % yield) was analysed by GC/MS and ^{1}H-NMR analysis.

The pyrolysis of compound **8** was performed at temperatures between 300°C and 950°C. At 750°C resulted a mixture of **8** (79%) and the unexpected isomer *cis* of 3-benzylidene phtalide (**11**, 18.5%) resulted. These compounds were not separated and the compound **11** was spectral characterized from this mixture:

^{1}H-NMR spectrum ($CDCl_3$, δ ppm, J Hz): 6.42 (s; H^1); 7.31(tt; 7.9; 1.5; 1H; H^{11}); 7.41 (t; 7.9; 2H; H^{10}; H^{12}); 7.53 (td; 1.4; 7.9; 1H; H^6); 7.71(td; 7.9; 1.2; H^5);7.85 (dd; 7.1; 1.5; 2H; H^9; H^{13}); 7.76 (dd; 7.8; 1.1; 1H; H^7); 7.93 (dd; 7.7; 1.1; 1H; H^4).

^{13}C-NMR spectrum ($CDCl_3$, δ ppm, J Hz): 166.95 (C^3); 144.41 (C$_q$); 140.43 (C$_q$); 134.61 (CH); 133.01(C$_q$); 131.12

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(C_q); 129.99 (CH); 128.88 (CH); 128.64 (CH); 128.33 (CH); 125.30 (CH); 123.07 (C_q); 119.94 (CH); 107.26 (CH).

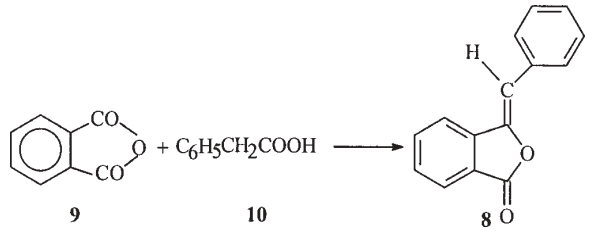
Mass spectrum (m/z; relative abundance %):50 (3); 89 (3); 164 (6);165 (8); 166 (5); 193 (7); 194 (8); 222 (100; B.P.; M); 223 (18; M+1); 224 (1; M+2).

At 950°C the GC/MS analysis indicated that the pyrolysis of **8** afforded four significant reaction products (**12-15,** see Scheme 1) separated by liquid chromatography on an Al_2O_3 (Merck-90; activity II) column, using petroleum ether (b.p. 30-35°C) and diethylether as solvents. With petroleum ether as eluent, phenanthrene (**12,** m.p.100°C); was isolated with a mixture of the petroleum ether and diethylether (95:5 vol), fluorenone (**13**, m.p. 83°C) and anthraquinone (**14**, m.p. 286°C) were obtained as a white solids; finaly, with diethylether, anthracene (**15**, m.p. 216°C) was separated.

The IR, ^{1}H-NMR and ^{13}C-NMR spectral data of the compounds **12 – 15** were identical with those described in lit.[10].

Results and discussions

3-(Phenylmethylene)-1(3H)-isobenzofuranone (3-benzylidenephtalide) (**8**) was obtained by the procedure described in lit.[9] (experimental).

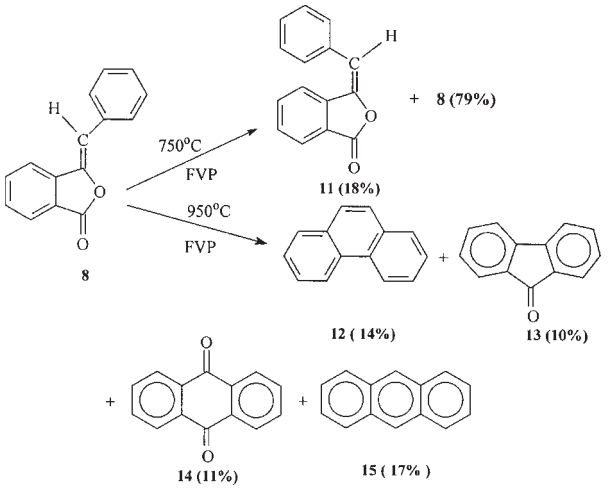


The flow-vacuum pyrolysis of phtalide **8** were performed in the same apparatus and in the similar conditions used before in our studies (Experimental: 1 Torr, 4mL/min argon flow-rate, large interval of temperatures: 300 and 950°C).

The phtalide **8** proved a remarkable thermal stability remaining unconverted between 300°C and 750°C.

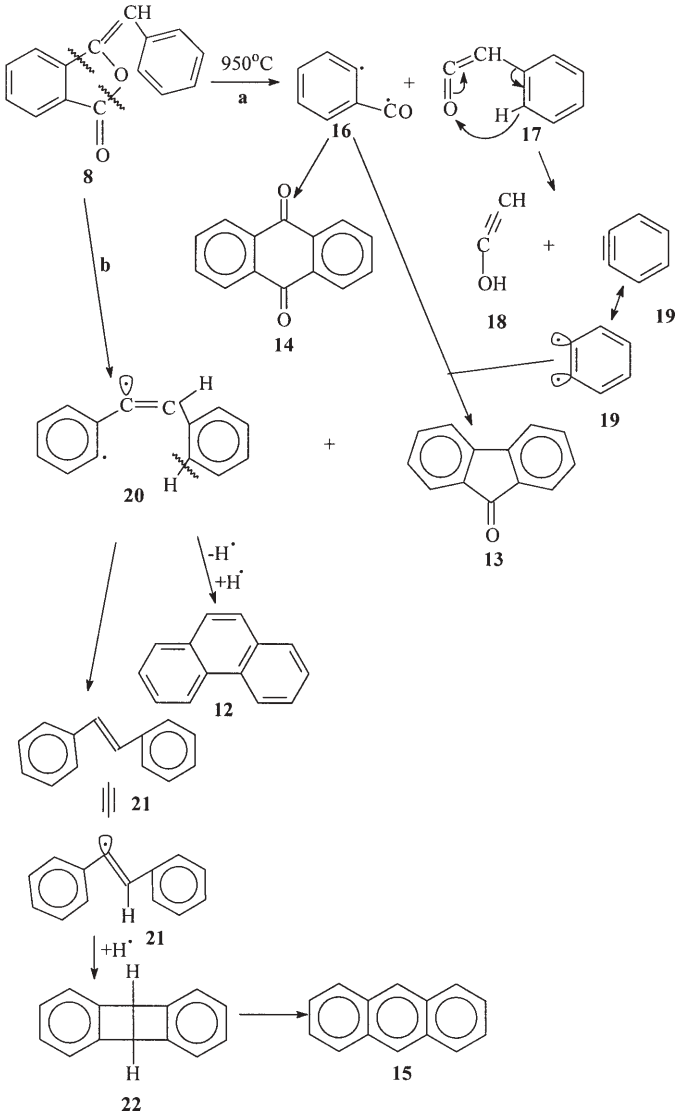
At 750, a mixture of two compounds: **8** (79% untransformed) and the unexpected his *cis* isomer **11**(18.5%)° resulted whereas at 950°C it was only 30% unconverted to pyrolysis products. The products distribution (scheme 1) was determined by GC/MS analyses.

The main reaction products were separated by preparative liquid chromatography on neutral alumina (Merck 90-activity II) using petroleum ether (b.p. 30-35°C):diethylether mixtures as eluents.



Scheme 1

The suggested reaction mechanism for pyrolysis of **8** is presented in scheme 2. The route **a**) involving a lactone bond break is a common thermal reaction which affords the diradical benzoyl **16** and the unstable intermediate compound **17.** The diradical **16** may be stabilized also by dimerzation affording anthraquinone (**14**) or by reaction with benzyne (**19**) forming fluorenone (**13**)**.**



Scheme 2

In the route **b**) the compound **8** loses a CO_2 molecule and form the diradical **20** which is stabilized by hydrogen atom migration affording phenanthrene (**12**) and anthracene(**15**).

Conclusions

In this work we have proved that:

- The compound **8** has a pronounced thermal stability until 750°C in conditions of flow-vacuum pyrolysis.
- The primary pyrolysis product is unexpected *cis* isomer **11** observed at 750°C (18%).
- The pyrolysis products at high temperatures are expected aromatic compounds **12** – **15**.
- A radical reaction mechanism is suggested in order to rationalize the formation of the pyrolysis reaction products.

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